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R32D9C R32E2A R32E2B R32E2DX R32E2Y R32E8  
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R32H5B2 R32H8 R32J2F R32J2Y R32J3A R32J3Y  
R32KC R32KE R32KJ R32S R32T2X R37N5  
C3W W229 W301 W318  
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(54) Curable compositions and method of curing same

(57) A curable composition comprises:

- (i) a resin (I) having an alkoxysilane and/or hydroxysilane group and oxirane group and obtained by reacting a resin (A) having a group selected from an isocyanate, hydroxyl, oxirane, carboxyl and amino group with a compound (a) having a group reactive with the functional group of the resin (A), and an alkoxysilane and/or hydroxysilane group and with a compound (b) having a group reactive with the functional group of the resin (A) and oxirane group, or
- (ii) a mixture of a resin (II) having an alkoxysilane group and/or hydroxysilane group and obtained by reacting the resin (A) with the compound (a) and a resin (III) having oxirane group and obtained by reacting a resin (B) having a group selected from an isocyanate, hydroxyl, carboxyl and amino group with the compound (b), and
- (iii) a chelate compound, as a crosslinking curing agent. The composition is curable at a temperature of up to 100°C in the presence of water.

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CURABLE COMPOSITIONS AND METHOD OF CURING SAME

The present invention relates to novel curable compositions and a method of curing the same.

Compositions are already known which are prepared by admixing an acid, base, organometallic catalyst or the like with an alkoxy silane-containing vinyl polymer and which can be cured by crosslinking at a relatively low temperature, i.e., at room temperature to 100°C. For example, Unexamined Japanese Patent Publication SHO 60-67553 discloses a composition which comprises a vinyl polymer containing an alkoxy silane, such as methacryloxypropyltrimethoxy silane, and an aluminum chelate compound admixed with the polymer.

However, the conventional composition has drawbacks. Since the hydroxy silane group produced by the hydrolysis of the alkoxy silane is the sole crosslinking functional group, the composition requires a large quantity of water for curing. Consequently, large amounts of by-products, such as alcohol, resulting from the hydrolysis give impaired properties to the cured product. Further when the composition is cured in the presence of only the water in air, the composition is cured only over the surface in contact with air, with its interior remaining almost uncured, so that the difference

between the surface and the interior in the degree of curing is liable to result in a shrunk product on curing.

An object of the present invention is to provide a novel composition which can be fully cured with a small amount of water and a method of curing the composition.

Another object of the invention is to provide a novel composition for affording a cured product of excellent properties and a method of curing the composition.

Another object of the invention is to provide a novel composition which is curable only with the water in air with a reduced difference between the surface and the interior in the degree of curing without shrinkage and a method of curing the composition.

These and other objects of the invention will become apparent from the following description.

The present invention provides a curable composition characterized in that the composition comprises:

- (i) a resin (I) having an alkoxysilane group and/or hydroxysilane group and oxirane group and obtained by reacting a resin (A) having at least one functional group selected from among an isocyanate group, hydroxyl group, oxirane group, carboxyl group and amino group with a compound (a) having a functional group

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- complementary to and reactive with the functional group of the resin (A), and an alkoxysilane group and/or hydroxysilane group and with a compound (b) having a functional group complementary to and reactive with the functional group of the resin (A) and oxirane group, or
- (ii) a mixture of a resin (II) having an alkoxysilane group and/or hydroxysilane group and obtained by reacting the resin (A) with the compound (a) and a resin (III) having oxirane group and obtained by reacting a resin (B) having at least one functional group selected from among an isocyanate group, hydroxyl group, carboxyl group and amino group with the compound (b), and
- (iii) a chelate compound serving as a crosslinking curing agent and admixed with the resin (I) or the mixture.

The invention also provides a curing method characterized in that the composition is cured at a temperature of up to 100°C in the presence of water.

The present inventor has conducted intensive research to overcome the drawbacks of the conventional composition disclosed in the foregoing publication and discovered the following novel findings.

- (1) The presence of the resin having an alkoxysilane group and/or hydroxysilane group and oxirane group makes not only the hydroxysilane group but also the oxirane

group serviceable as a crosslinking functional group, with the result that the composition is fully curable in the presence of a small amount of water.

(2) The composition, when cured, produces only greatly reduced amounts of alcohol and like by-products, giving a cured product exhibiting excellent properties almost free of impairment.

(3) When the composition is cured in the presence of only the water in air, the hydroxysilane in the surface of the composition in contact with air undergoes a crosslinking reaction, which induces oxirane to undergo a crosslinking reaction throughout the interior in a chainlike fashion, consequently causing no shrinkage due to a reduced difference between the surface and the interior in the degree of curing.

The present invention has been accomplished based on these novel findings.

There are two types of curable compositions of the invention: one comprising the component (i) and a chelate compound serving as a crosslinking curing agent and admixed therewith, and the other comprising the component (ii) and the chelate compound.

The component (i) of the former curable composition of the invention, i.e., the resin (I) has an alkoxysilane group and/or hydroxysilane group and oxirane

group and obtained by reacting a resin (A) having at least one functional group selected from among an isocyanate group, hydroxyl group, oxirane group, carboxyl group and amino group with a compound (a) having a functional group complementary to and reactive with the functional group of the resin (A), and an alkoxysilane group and/or hydroxysilane group and with a compound (b) having a functional group complementary to and reactive with the functional group of the resin (A) and oxirane group.

The wording "a functional group complementary to and reactive with the functional group of the resin (A)" as herein used means that these groups can be reacted with and bonded to each other.

Examples of combinations of such complementary functional groups according to the invention are hydroxyl/isocyanate, hydroxyl/alkoxysilane, hydroxyl/hydroxysilane, hydroxyl/carboxyl, isocyanate/amino, isocyanate/mercapto, isocyanate/carboxyl, oxirane/carboxyl, oxirane/amino and the like.

Examples of preferred combinations of the functional group of the resin (A)/the functional group of the compound (a) or (b) complementary to each other for giving the resin (I) are hydroxyl/alkoxysilane, hydroxyl/hydroxysilane, hydroxyl/isocyanate,

isocyanate/hydroxyl and the like.

Typically, the resin (I) can be prepared, for example, by:

- (1) reacting a hydroxyl-containing resin with a compound containing an alkoxysilane group and/or hydroxysilane group or an isocyanate-containing alkoxysilane compound as the compound (a) and an isocyanate-containing oxirane compound as the compound (b),
- (2) reacting an isocyanate-containing resin with a hydroxyl-containing alkoxysilane compound as the compound (a) and a hydroxyl-containing oxirane compound as the compound (b),
- (3) reacting an isocyanate-containing resin with a hydroxyl-containing oxirane compound as the compound (b) to obtain an oxirane-containing urethane resin, subjecting some of the oxirane groups of the resin to ring cleavage with an alcohol to introduce hydroxyl into the resin, and reacting the resulting product with a compound containing an alkoxysilane group and/or hydroxysilane group as the compound (a), or like process.

The resins obtained by these methods (1) to (3) are those having a urethane bond and having introduced therein the alkoxysilane group and/or hydroxysilane group

or the oxirane group by the urethane bond.

The "hydroxyl-containing resin" to be used in these processes (1) to (3) is a known resin containing a hydroxyl group reactive with the alkoxysilane group and/or hydroxysilane group and isocyanate group. Examples of such resins are acrylic resin, polyester, polyether, polyurethane, polyetherurethane, polyesterurethane and the like.

Examples of "isocyanate-containing resins" are an adduct of the hydroxyl-containing resin with a diisocyanate compound, preferably such as tolylene diisocyanate, xylylene diisocyanate, hydrogenated product of such a diisocyanate, or isophorone diisocyanate, in the ratio of one mole of the diisocyanate compound per mole of hydroxyl; a homopolymer of an isocyanate-containing unsaturated monomer such as an equimolar adduct of isophorone diisocyanate or tolylene diisocyanate with a hydroxyalkyl (meth)acrylate such as 2-hydroxyethyl (meth)acrylate, m-isopropenyl- $\alpha,\alpha$ -dimethylbenzyl isocyanate or isocyanoethyl (meth)acrylate or a copolymer of the monomer and an aromatic vinyl monomer, alkyl (meth)acrylate or the like; etc.

Examples of "compounds containing an alkoxysilane group and/or hydroxysilane group" are a compound containing an alkoxysilane group and/or



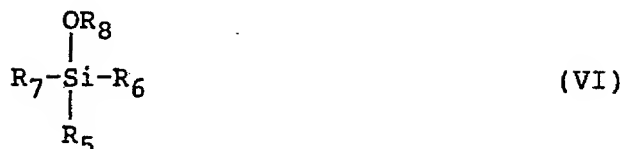
hydroxysilane group reactive with the hydroxyl group of the hydroxy-containing resin, hydroxysilane-containing compound obtained by hydrolyzing an alkoxysilane-containing compound in the presence of an acid or water as a catalyst, a low condensation product of this compound, etc. Examples of useful alkoxysilane-containing compounds are those represented by the following formulae.



wherein  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  are the same or different and are each a hydrogen atom, alkyl having 1 to 12 carbon atoms, or cycloalkyl having 3 to 12 carbon atoms, and  $\text{R}_5$  and  $\text{R}_6$  are the same or different and are each alkyl having 1 to 12 carbon atoms, cycloalkyl having 3 to 12 carbon atoms or phenyl.

Examples of "isocyanate-containing alkoxysilane compounds" are those represented by the following

formulae.

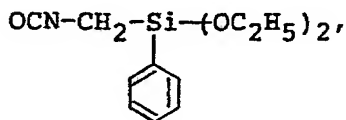
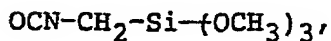
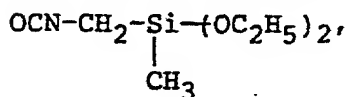
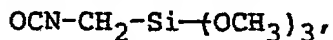
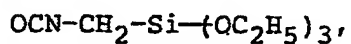
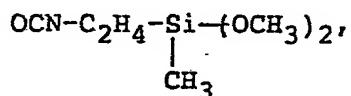
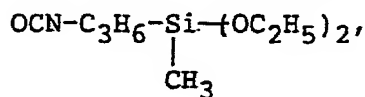
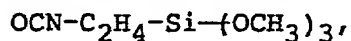
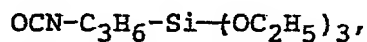


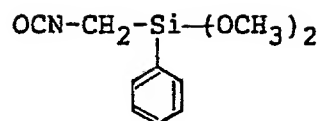
wherein  $\text{R}_5$  and  $\text{R}_6$  are as defined above,  $\text{R}_7$  is a hydrocarbon group having 1 to 12 carbon atoms and substituted with an isocyanate group, or an isocyanate group, and  $\text{R}_8$ ,  $\text{R}_9$  and  $\text{R}_{10}$  are the same or different and are each alkyl having 1 to 12 carbon atoms or cycloalkyl having 3 to 12 carbon atoms.

Examples of alkyl groups or cycloalkyl groups in the above formulae are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, decyl, undecyl, dodecyl, cyclopropyl, cyclobutyl, cyclohexyl and the like.  $\text{R}_1$  to  $\text{R}_4$  and  $\text{R}_8$  to  $\text{R}_{10}$  bonded to the oxygen atom in the formulae (I) to (VI) are preferably lower alkyl having 1 to 6 carbon atoms since a highly curable coating can then be obtained.

Examples of compounds of the formulae (I) to (III) are tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetrabutoxysilane, trimethoxymethylsilane, triethoxymethylsilane, tributoxymethylsilane, tributoxyethylsilane, trimethoxybutylsilane, triethoxycyclohexylsilane, dimethoxydimethylsilane, diethoxydimethylsilane, diethoxydiethylsilane, dipropoxydiethylsilane, diethyldihydroxysilane, dihexyldihydroxysilane, methyltrihydroxysilane, phenyltrihydroxysilane, tetrahydroxysilane and the like.

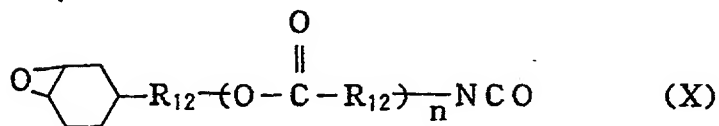
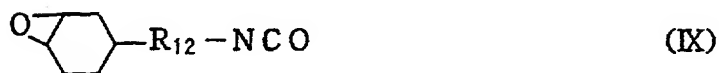
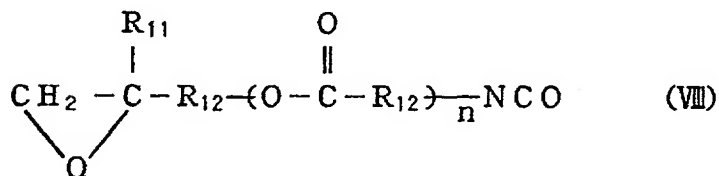
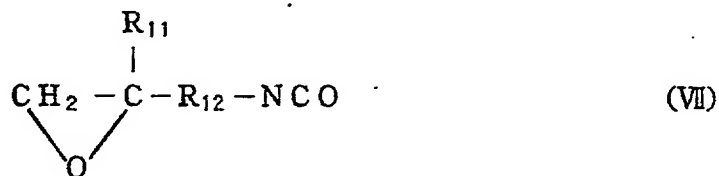
Examples of compounds of the formula (IV) to (VI) are

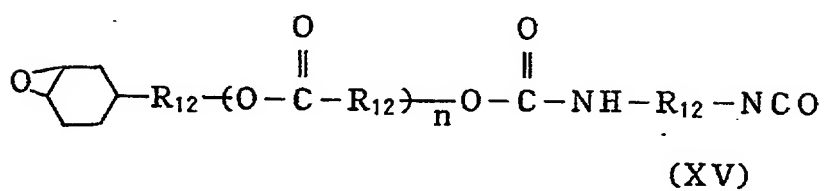
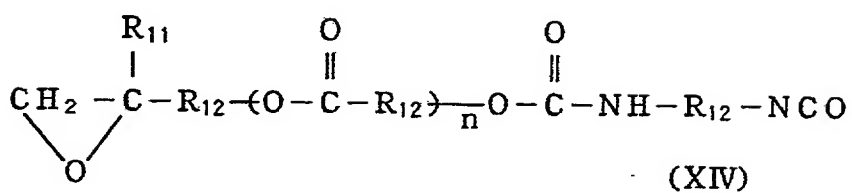
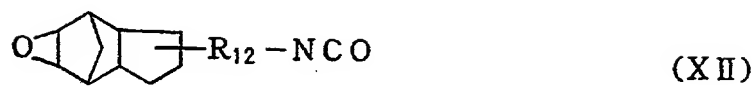
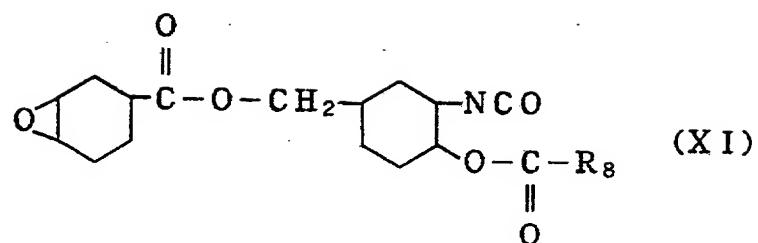




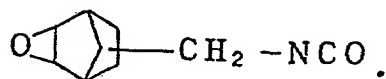
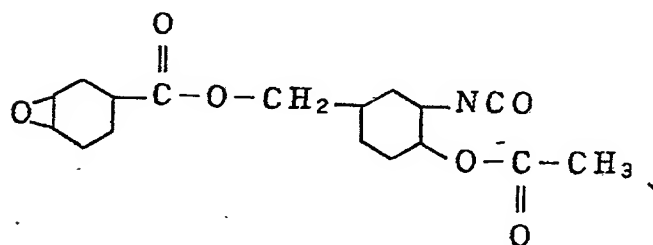
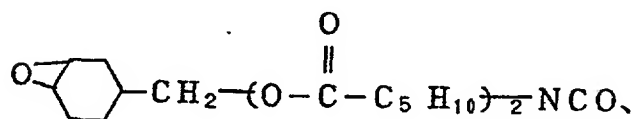
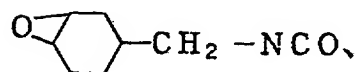
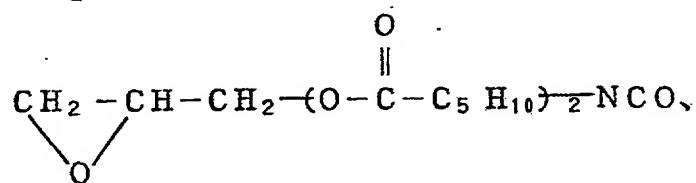
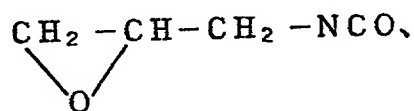
and the like.

The "isocyanate-containing oxirane compound" is an oxirane compound having an isocyanate group reactive with the hydroxyl group of the hydroxyl-containing resin. Examples of such compounds are those of the following formula.





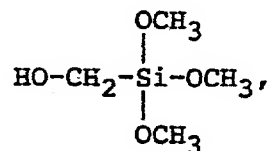
wherein  $R_8$  is as defined above,  $R_{11}$  is a hydrogen atom or methyl,  $R_{12}$  is a hydrocarbon group having 1 to 12 carbon atoms and the  $R_{12}$  groups are the same or different, and  $n$  is an integer of 1 to 10. Examples of hydrocarbon groups represented by  $R_{12}$  and having 1 to 12 carbon atoms are those corresponding to the above-mentioned alkyl groups with 1 to 12 carbon atoms but smaller than these groups by one in the number of hydrogen atoms. More specific examples of compounds of the formulae (VII) to (XV) are those represented by the following formulae.

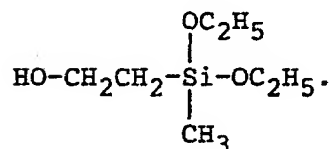
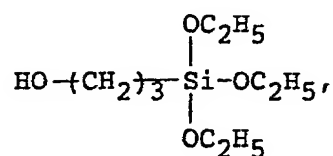
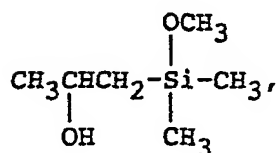
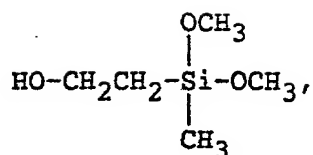


The "hydroxyl-containing alkoxy silane compound" is one having an alcoholic hydroxyl group reactive with an isocyanate group. Examples of such compounds are

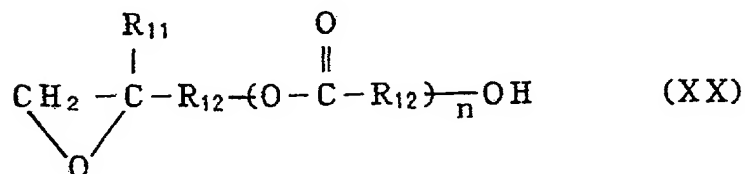
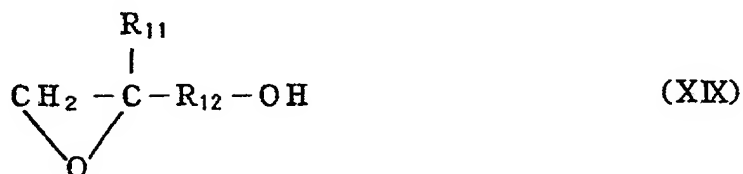


wherein  $\text{R}_8$ ,  $\text{R}_9$  and  $\text{R}_{10}$  are as defined above,  $\text{R}_{13}$  is a hydrocarbon group having 1 to 12 carbon atoms and substituted with hydroxyl. The hydrocarbon group represented by  $\text{R}_{13}$  and having 1 to 12 carbon atoms is the same as the above-mentioned one. More specific examples of compounds of the formula (XVI) to (XVIII) are as follows.

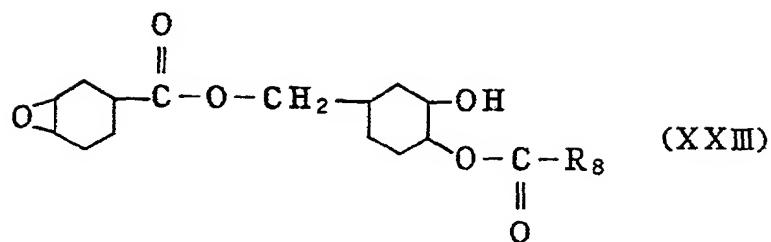
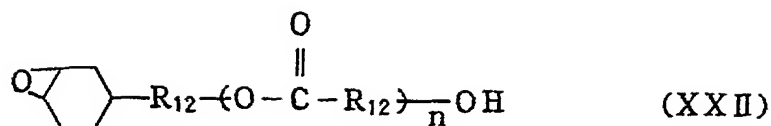




The "hydroxyl-containing oxirane compound" is one having an alcoholic hydroxyl group reactive with an isocyanate group. Examples of such compounds are those represented by the following fomulae.







wherein  $\text{R}_8$ ,  $\text{R}_{11}$ ,  $\text{R}_{12}$  and  $n$  are as defined above.

In the processes (1) to (3), the reaction of the hydroxyl group with the alkoxysilane and/or hydroxysilane and isocyanate groups (process (1)), and the reaction of the isocyanate group with the hydroxyl group (processes (2) and (3)) can be carried out by known method. For example, these reactions can be conducted by dissolving or dispersing the mixture of compounds having the functional groups mentioned in a organic solvent such as xylene, toluene, ethyl acetate, propyl acetate, methyl ethyl

ketone, methyl isobutyl ketone or heptane, and reacting the solution or dispersion usually at about 40 to about 150°C for about 1 to about 10 hours.

From the viewpoint of the properties of the cured product to be obtained, the resin (I) prepared by one of the processes (1) to (4) for use in the present invention is preferably one having introduced therein an alkoxysilane group and/or hydroxysilane group or oxirane group by a urethane bond.

The oxirane group of the resin (I) for use in the present invention is preferably an alicyclic oxirane group since the oxirane group is then highly reactive when subjected to ring-cleavage polymerization reaction, resulting in expedited curing and giving improved properties to the coating on curing.

The resin (I) to be used in the invention can be one containing about 0.01 to about 10 moles of alkoxy-silane and/or hydroxysilane and about 0.1 to about 10 moles of oxirane per kilogram of the resin as functional groups. With less than about 0.01 mole of alkoxysilane and/or hydroxysilane present, reduced curability will result, making it impossible to obtain a coating which is excellent in physical and chemical properties. On the other hand, if the amount more than about 10 moles, the composition is prone to the influence of water in air,

failing to cure uniformly and giving a poor finish to the coating. Further with less than about 0.1 mole of oxirane present, the coating is liable to shrink and exhibits impaired properties, hence undesirable. On the other hand, it is technically difficult to introduce into the resin more than about 10 moles of oxirane, which further results in impaired curability.

The molecular weight of the resin (I), which varies depending on the kind of resin, can be suitably determined according to the properties required of the coating to be formed and can be usually about 1000 to about 100000, preferably about 2000 to about 20000, in GPC peak molecular weight.

Next, the resins (II) and (III) will be described which are used in the curable composition of the invention comprising the component (ii) and a chelate compound serving as a crosslinking curing agent and admixed therewith.

The resin (II) for use in the present composition is a resin having an alkoxysilane group and/or hydroxysilane group and obtained by reacting the resin (A) with the compound (a).

Examples of preferred combinations of the functional group of the resin (A)/the functional group of the compound (a) complementary to each other for giving

the resin (II) are hydroxyl/isocyanate, hydroxyl/carboxyl, hydroxyl/alkoxysilane, hydroxyl/hydroxysilane, isocyanate/hydroxyl, isocyanate/mercapto, isocyanate/carboxyl, isocyanate/amino, oxirane/carboxyl, oxirane/amino, carboxyl/isocyanate, carboxyl/hydroxyl, carboxyl/oxirane, amino/isocyanate, amino/oxirane and the like.

Typically, the resin (II) can be prepared, for example, by:

- (1) reacting a hydroxyl-containing resin with the above-mentioned compound containing an alkoxysilane group and/or hydroxysilane group,
- (2) reacting a hydroxyl-containing resin with an isocyanate-containing alkoxysilane compound,
- (3) reacting an isocyanate-containing resin with the above-mentioned hydroxyl-containing alkoxysilane compound,
- (4) reacting an isocyanate-containing resin with at least one of an amino-containing alkoxysilane compound (such as N-phenyl- $\gamma$ -aminopropyltrimethoxysilane) and a mercapto-containing alkoxysilane compound (such as  $\gamma$ -mercaptopropyltrimethoxysilane),
- (5) reacting an oxirane-containing resin with at least one of the above amino-containing alkoxysilane compound, a carboxyl-containing alkoxysilane compound

(such as trimethoxysilylbenzoic acid) and the above mercapto-containing alkoxy silane compound,

- (6) reacting a carboxyl-containing resin with at least one of a glycidyl-containing alkoxy silane compound (such as  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -glycidoxypropyldiethoxysilane, or  $\beta$ -(3,4-epoxycyclohexyl)ethyltrimethoxysilane), the above hydroxyl-containing alkoxy silane compound and the above isocyanate-containing alkoxy silane compound,
- (7) reacting an amino-containing resin with at least one of the above isocyanate-containing alkoxy silane compound and the above glycidyl-containing alkoxy silane compound, or like process.

The process (2) or (3) gives a urethane-containing resin.

The "hydroxyl-containing resin" and "isocyanate-containing resin" for use in these processes (1) to (7) can be the same resins as already mentioned. The "oxirane-containing resin" is, for example, a polymer consisting essentially of an unsaturated monomer such as glycidyl (meth)acrylate. Examples of "carboxyl-containing resins" are a polymer consisting essentially of a carboxyl-containing unsaturated monomer, such as (meth)acrylic acid or maleic acid, and a polyester resin obtained by esterifying a polybasic acid (such as phthalic

acid, isophthalic acid or terephthalic acid) with a polyhydric alcohol (such as ethylene glycol, polyethylene glycol, neopentyl glycol, 1,6-hexanediol or trimethylolpropane). The "amino-containing resin" is, for example, a resin prepared by reacting the above polybasic acid with an amino-containing compound such as propanolamine, monoethanolamine, diethanolamine, ethylenediamine or the like.

The resin (II) can be prepared by subjecting the resin (A) and the compound (a) with their respective functional groups to a known reaction such as ring-cleavage reaction, addition reaction or condensation reaction.

The resin (II) thus obtained can be one containing about 0.01 to about 10 moles of alkoxysilane and/or hydroxysilane per kilogram of the resin. With less than about 0.01 mole of alkoxysilane and/or hydroxysilane present, reduced curability will result, failing to give a coating having excellent chemical properties. With more than 10 moles of alkoxysilane and/or hydroxysilane present, the resin (II) has reduced compatibility with the oxirane-containing resin (III), giving lower stability to the mixture.

The resin (III) for use in the curable composition of the invention is a resin having an oxirane

group and obtained by reacting a resin (B) having at least one of isocyanate group, hydroxyl group, carboxyl group and amino group as a functional group with the compound (b).

Typically, the resin (III) can be prepared, for example, by:

- (1) reacting the above-mentioned isocyanate-containing resin with the above hydroxyl-containing oxirane compound,
- (2) reacting the above hydroxyl-containing resin with the above isocyanate-containing oxirane compound,
- (3) reacting the above amino-containing resin with the above isocyanate-containing oxirane compound, or like process.

The process (1) or (2) gives a urethane-containing resin.

Examples of preferred combinations of the functional group of the resin (B)/the functional group of the compound (b) complementary to each other for giving the resin (III) are isocyanate/hydroxyl, amino/isocyanate, hydroxyl/isocyanate, carboxyl/oxirane and the like.

In preparing the resin (III), it is desirable to use a compound having an alicyclic oxirane group since the oxirane group is highly reactive to result in expedited curing and give improved properties to the

coating on curing.

The resin (III) can be prepared by subjecting the resin (B) and the compound (b) with their respective functional groups to a known process of addition reaction.

The resin (III) thus obtained can be one containing about 0.1 to about 10 moles of oxirane per kilogram of the resin. With less than about 0.1 mole of oxirane present, poor properties will result, whereas with more than 10 moles of oxirane present, impaired curability tends to result. It is also difficult to introduce such a large amount of oxirane into the resin.

An epoxy resin such as bisphenol A, bisphenol F or novolak epoxy resin, if used in the invention in place of the resin (III), is low in compatibility with the resin (II), failing to give coatings having an excellent finish and good weather resistance.

The molecular weight of the resin (II) as well as the resin (III) is usually 500 to 100000, preferably 750 to 30000, in number average molecular weight, although variable depending on the kind of resin and the properties of the coating to be formed.

The proportions of the resins (II) and (III) are, based on the combined amount thereof, 5 to 95 wt.%, preferably 20 to 80 wt.%, of the resin (II) and 95 to 5 wt.%, preferably 80 to 20 wt.%, of the resin (III). If



less than 5 wt.% of the resin (II) is used with more than 95 wt.% of the resin (III), lower curability will result, whereas if more than 95 wt.% of the resin (II) is used with less than 5 wt.% of the resin (III), lower curability will result to give a cured product of poor properties, hence undesirable.

According to the present invention, a chelate compound is used as a crosslinking curing agent. It is desirable to use as the compound at least one of an aluminum chelate compound, titanium chelate compound and zirconium chelate compound. Of these chelate compounds, more preferable are those containing a compound capable of forming a keto-enol tautomer, as ligands forming a stable chelate ring.

Examples of useful compounds capable of forming a keto-enol tautomer are  $\beta$ -diketones (such as acetylacetone), acetoacetic acid esters (such as methyl acetoacetate), malonic esters (such as ethyl malonate), ketones having hydroxyl in the  $\beta$ -position (such as diacetone alcohol), aldehydes having hydroxyl in the  $\beta$ -position (such as salicylaldehyde), esters having hydroxyl in the  $\beta$ -position (such as methyl salicylate), etc. Especially preferred results can be achieved when acetoacetates and  $\beta$ -diketones are used.

The aluminum chelate compound can be prepared

advantageously, for example, by admixing the compound capable of forming a keto-enol tautomer with an aluminum alcoholate represented by the formula



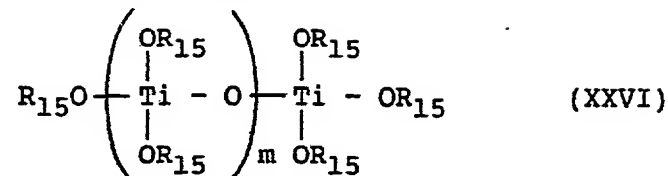
wherein  $\text{R}_{14}$  is the same or different and represents alkyl having 1 to 20 carbon atoms or alkenyl, usually in the ratio of up to about 3 moles of the former per mole of the latter, and heating the mixture when required.

Examples of alkyl groups having 1 to 20 carbon atoms are the aforementioned alkyl groups having 1 to 12 carbon atoms, tridecyl, tetradecyl, octadecyl and the like. Examples of alkenyl groups are vinyl, allyl and the like.

Examples of aluminum alcoholates represented by the formula (II) are aluminum trimethoxide, aluminum triethoxide, aluminum tri-n-propoxide, aluminum triisopropoxide, aluminum tri-n-butoxide, aluminum triisobutoxide, aluminum tri-sec-butoxide, aluminum tri-tert-butoxide, etc. It is especially desirable to use aluminum triisopropoxide, aluminum tri-sec-butoxide and aluminum tri-n-butoxide.

The titanium chelate compound can be prepared advantageously, for example, by admixing the compound capable of forming a keto-enol tautomer with a titanate

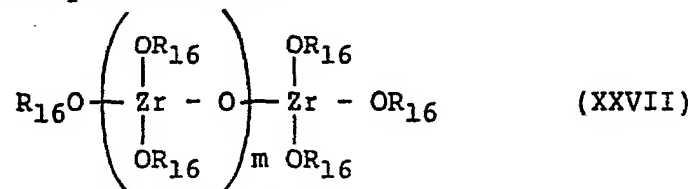
represented by the formula



wherein m is an integer of 0 to 10, and R<sub>15</sub> is the same or different and represents alkyl having 1 to 20 carbon atoms or alkenyl, usually in the ratio of up to about 4 moles of the former per mole of the Ti in the titanate, followed by heating when required. Examples of alkyl groups having 1 to 20 carbon atoms and alkenyl groups are the same as those given above.

Examples of titanates represented by the formula (XXVI) wherein m is 0 are tetramethyl titanate, tetraethyl titanate, tetra-n-propyl titanate, tetraisopropyl titanate, tetra-n-butyl titanate, tetraisobutyl titanate, tetra-tert-butyl titanate, tetra-n-pentyl titanate, tetra-n-hexyl titanate, tetraisooctyl titanate, tetra-n-lauryl titanate and the like. Favorable results can be obtained by using tetraisopropyl titanate, tetra-n-butyl titanate, tetraisobutyl titanate and tetra-tert-butyl titanate. Of the titanates wherein m is 1 or greater, the dimers to hendecamers (m = 1 to 10 in the formula (XXVI)) of tetraisopropyl titanate, tetra-n-butyl titanate, tetraisobutyl titanate and tetra-tert-butyl titanate achieve good results.

The zirconium chelate compound can be prepared favorably, for example, by admixing the compound capable of forming a keto-enol tautomer with a zirconate represented by the formula



wherein m is an integer of 0 to 10, and  $R_{16}$  is the same or different and represents alkyl having 1 to 20 carbon atoms or alkenyl, usually in the ratio of up to about 4 moles of the former per mole of the Zr in the zirconate, followed by heating when required. Examples of alkyl groups with 1 to 20 carbon atoms and alkenyl groups are the same as those exemplified above.

Examples of zirconates represented by the formula (XXVII) wherein m is 0 are tetraethyl zirconate, tetra-n-propyl zirconate, tetraisopropyl zirconate, tetra-n-butyl zirconate, tetra-sec-butyl zirconate, tetra-tert-butyl zirconate, tetra-n-pentyl zirconate, tetra-tert-pentyl zirconate, tetra-tert-hexyl zirconate, tetra-n-heptyl zirconate, tetra-n-octyl zirconate, tetra-n-stearyl zirconate and the like. Especially good result can be obtained with use of tetraisopropyl zirconate, tetra-n-propyl zirconate, tetraisobutyl zirconate, tetra-n-butyl zirconate, tetra-sec-butyl zirconate and tetra-tert-butyl

zirconate. Of the zirconates wherein  $m$  is 1 or greater, the dimers to hendecamers ( $m = 1$  to 10 in the formula (XXVII)) of tetraisopropyl zirconate, tetra-*n*-propyl zirconate, tetra-*n*-butyl zirconate, tetraisobutyl zirconate, tetra-*sec*-butyl zirconate and tetra-*tert*-butyl zirconate give good results. The chelate compound may contain structural units wherein such zirconates are associated with each other.

Examples of especially preferred chelate compounds for use in the invention are aluminum chelate compounds such as diisopropoxy ethylacetoacetate aluminum, tris(ethylacetoacetate)aluminum, tris(*n*-propylacetoacetate)aluminum, tris(isopropylacetoacetate)aluminum, tris(*n*-butylacetoacetate)aluminum, isopropoxy bis(ethylacetoacetate)aluminum, isopropoxy bis(propionylacetonato)aluminum, tris(acetylacetonato)aluminum, tris(propylacetoacetate)aluminum, tris(propionylacetonato)aluminum, acetylacetonato-bis(ethylacetoacetate)aluminum, ethylacetoacetate bis(acetylacetonato)aluminum, tris(isopropionylacetonato)aluminum, tris(*sec*-butyrylacetonato)aluminum, [bis(isopropionylacetonato) *sec*-butyrylacetonato]aluminum and tris(butylacetoacetate)aluminum; titanium chelate compounds such as diisopropoxy-bis(ethylacetoacetate)titanate, diisopropoxy-bis(acetylacetonato)titanate and isopropoxy-tris(propionyl-

acetonato)titanate; and zirconium chelate compounds such as tetrakis(acetylacetonato)zirconium, tetrakis(n-propylacetoacetate)zirconium, tetrakis(propionylacetonato)zirconium and tetrakis(ethylacetoacetate)zirconium.

According to the present invention, one of the aluminum chelate compound, the zirconium chelate compound and the titanium chelate compound may be used, or at least two kinds of these compounds may be used in a suitable combination. It is suitable to use the crosslinking curing agent in an amount of about 0.01 to about 30 parts by weight per 100 parts by weight of the resin component (i) or (ii), calculated as solids. Amounts outside this range is not desirable; if the amount is smaller, reduced crosslinking curability will result, whereas if used in a larger amount, the curing agent remains in the cured product and tends to result in lower water resistance. The amount is preferably 0.1 to 10 parts by weight, more preferably 1 to 5 parts by weight.

When required, extender pigments, coloring pigments, dyes, etc. can be incorporated into the curable composition of the invention. Further when required, it is also possible to incorporate into the composition monofunctional or polyfunctional epoxy compounds, low-molecular-weight silane compounds such as triphenylmethoxy-silane and diphenyldimethoxysilane, common

alkoxysilane-containing silicone resins and other resins. Further to give improved storage stability, it is possible to add to the composition compounds providing ligands for the chelate compound, such as the aforementioned compounds capable of forming a keto-enol tautomer.

The present curable composition is suitable, for example, for use as a coating composition, adhesive, ink, etc.

The present composition is easily curable by crosslinking at low temperatures of up to 100°C in the presence of water. More specifically, the composition of the invention can be fully cured usually in about 8 hours to about 7 days without necessitating any heating, merely by adding water to the composition and thereafter applying the composition, or by applying the composition and exposing the coating to air. Alternatively, when heated, for example, at 40 to 100°C, the composition is curable in about 5 minutes to about 3 hours. The water needed for curing is in such a small amount as the moisture content of air. When water is added to the composition before application, about 0.1 to about 1 wt.% of water usually produces a satisfactory result.

The resin composition of the present invention is readily curable through crosslinking at low temperature

in the presence of a small quantity of water, presumably for the following reason. For example, when the zirconium chelate compound is present, the alkoxyl groups in the resin hydrolyze in the first stage in the presence of water under the catalytic action of the zirconium chelate compound to produce hydroxysilane groups. In the next second stage, hydroxysilane groups undergo dehydration condensation for crosslinking or react with the zirconium chelate compound to form  $-\overset{|}{\text{Si}}-\text{O}-\overset{|}{\text{Zr}}-\text{O}-\overset{|}{\text{Si}}-$  bonds for crosslinking. In the third stage,  $-\overset{|}{\text{Si}}-\text{O}-\overset{|}{\text{Zr}}-$  bonds are coordinated to other hydroxysilane groups to polarize these groups, whereupon the polarized groups cause ring-cleavage polymerization of the oxirane groups in the resin.

The conventional curable composition of the same type as the present composition cures through the second stage reaction only, whereas the oxirane groups introduced into the resin component of the present composition permit the second stage reaction and the third stage reaction to proceed concurrently in a chainlike fashion, whereby the composition is crosslinked for curing. Presumably for this reason, the present composition is favorably curable at a low temperature in the presence of a small amount of water.

The curable composition of the present invention



comprises a resin component containing an alkoxysilane group and/or hydroxysilane group and oxirane group, and a chelate compound as a crosslinking curing agent, so that the composition has the outstanding advantages given below.

(1) The composition can be easily crosslinked for curing at a low temperature of up to 100°C in the presence of a small amount of water, e.g., the moisture in air.

(2) Crosslinking through the above-mentioned condensation reaction, etc. and crosslinking through the ring-cleavage reaction proceed concurrently, consequently diminishing the difference in the degree of curing between the surface and the interior to obviate shrinkage.

(3) Because of reduced amounts of alcohol and other by-products, the composition affords cured products which are excellent in properties, especially in resistance to water, weather and impact, amenability to top coating, flexibility and resistance to staining.

(4) The composition has high storage stability and remains stable for at least one year in the absence of water.

(5) When the resin used has a urethane bond, the cured product obtained is excellent in impact resistance, elongation and other properties.

The present invention will be described in


greater detail with reference to the following preparation examples, examples and comparative examples, in which the parts and percentages are all be weight unless otherwise specified.

Preparation of resin (I) having alkoxysilane group and/or hydroxysilane group and oxirane group

Preparation Example I-1

Phthalic anhydride	1480 parts
Neopentyl glycol	1155 parts

These compounds were placed in to a four-necked flask and subjected to dehydration condensation reaction at 220°C. When the acid value of the mixture reduced to not higher than 3, the reaction was terminated, whereupon the reaction mixture was diluted with 2455 parts of toluene to obtain a resin solution. The solution had a nonvolatile content of 50.0% and Gardner viscosity (at 25°C, the same as hereinafter) of P.

To the resin solution were added 444 parts of isophorone diisocyanate and 444 parts of toluene, and the mixture was reacted at 110°C for 3 hours. Subsequently, 192 parts of -CH<sub>2</sub>OH was added, and the mixture was reacted at 110°C for 2 hours. With addition of 31 parts of ethylene glycol, the mixture was further reacted at 110°C for 4 hours. When the NCO value of the mixture reduced to not higher than 5, the reaction was

terminated. To the reaction mixture were then added 99 parts of phenyl-trimethoxysilane and 0.1 part of p-toluenesulfonic acid. The mixture was reacted for about 5 hours until the temperature thereof reached 110°C to remove methanol. Toluene (275 parts) was thereafter added to the reaction mixture, giving a resin solution I, which was 49.7% in nonvolatile content and X in Gardner viscosity. The solution had 0.47 mole of oxirane group and 0.31 mole of methoxysilane group per kilogram of the resin solids and was 3200 in GPC peak molecular weight.

Preparation Example I-2

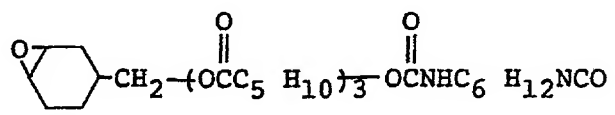
Into a four-necked flask were placed 850 parts of "Placel #208" (brand name, product of Daicel Ltd., polycaprolactone with terminal hydroxyl group, 850 in molecular weight), 555 parts of isophorone diisocyanate and 1400 parts of xylene, and the mixture was reacted at 130°C for 1 hour. The resin solution obtained was 50.3% in nonvolatile content and H in Gardner viscosity. To the solution were added 148 parts of glycidol and 148 parts of xylene, followed by reaction at 130°C for 5 hours to give a reaction mixture A. With addition of 31 parts of ethylene glycol, the mixture was reacted at 130°C for 3 hours. Further with addition of 68 parts of methyl-trimethoxysilane and 0.1 part of tris(acetylacetonato)-aluminum, the mixture was reacted for the removal of

methanol for about 3 hours until the temperature thereof reached 140°C. Subsequently, 52 parts of n-propanol was added to the reaction mixture to obtain a resin solution II, which was 50.0% in nonvolatile content, L in Gardner viscosity and 2000 in GPC peak molecular weight and had 1.2 moles of oxirane groups and 0.6 mole of methoxysilane group per kilogram of the resin solids.

Preparation Example I-3

2-Hydroxyethyl methacrylate	130 parts
n-Butyl methacrylate	870 parts
Azobisisobutyronitrile	30 parts

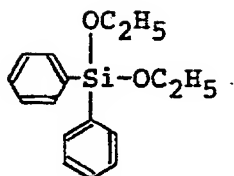
The above mixture was added dropwise to 667 parts of butyl acetate in a four-necked flask at 120°C over a period of 3 hours, and the resulting mixture was thereafter aged at 120°C for 3 hours, giving a resin solution which was 60.5% in nonvolatile content and G in Gardner viscosity. To the solution was added the following compounds.

	574 parts
Butyl acetate	383 parts

The mixture was reacted at 120°C for 5 hours. The reaction mixture was 60.2% in nonvolatile content and Q in Gardner viscosity.

The following compounds were then added to the

mixture.



27 parts

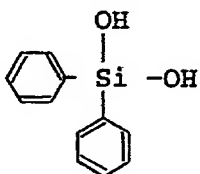
Tetrabutoxy titanate

0.02 part

The mixture was reacted for the removal of ethanol for about 5 hours until the temperature thereof reached 120°C, affording a resin solution III, which was 61.0% in nonvolatile content, Q in Gardner viscosity and 20000 in GPC peak molecular weight and contained 0.5 mole of oxirane group and 0.05 mole of ethoxysilane group per kilogram of the resin solids.

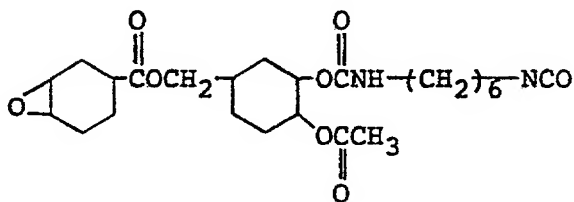
Preparation Example I-4

Tolylene diisocyanate (522 parts) and 2000 parts of polypropylene glycol with terminal hydroxyl group (500 in molecular weight) were placed into a four-necked flask and reacted at 80°C for 3 hours, giving a resin solution having a nonvolatile content of 100 % and a Gardner viscosity of Z<sub>2</sub>. To the solution was added 216 parts of the following compound.



The mixture was reacted at 180°C until the amount of water removed increased to 18 parts. The reaction mixture was 100 % in nonvolatile content and Z<sub>3</sub> in Gardner viscosity.

With addition of 480 parts of the compound



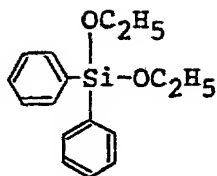
the mixture was further reacted until the NCO value thereof reduced to not higher than 5, giving a resin solution IV. The solution was 99.8% in nonvolatile content, Z<sub>5</sub> in Gardner viscosity and 3200 in GPC peak molecular weight and had 0.3 mole of oxirane group and 0.3 mole of hydroxysilane group per kilogram of the resin solids.

Preparation Example I-5

2-Hydroxyethyl methacrylate	130 parts
Glycidyl methacrylate	142 parts
n-Butyl methacrylate	728 parts
Azobisisobutyronitrile	30 parts

The above mixture was added dropwise to 667 parts of butyl acetate in a four-necked flask at 120°C over a period of 3 hours, and the resulting mixture was thereafter aged at 120°C for 3 hours. The resin solution obtained was 60.3% in nonvolatile content and P in Gardner

viscosity.



270 parts

Tetrabutoxy titanate

0.2 part

The above compounds were added to the solution, and the mixture was reacted for the removal of ethanol for about 5 hours until the temperature thereof increased to 120°C, whereby a resin solution V was obtained. This solution was 63.0% in nonvolatile content, Q in Gardner viscosity and 20000 in GPC peak molecular weight and had 0.79 mole of oxirane group and 0.79 mole of ethoxysilane group per kilogram of the resin solid.

Preparation Example I-6

Methyltrimethoxysilane (68 parts) was blended cold with 3100 parts of the reaction mixture A of Preparation Example II to obtain a resin solution VI.

Example 1-8 and Comparative Examples 1-3

Compositions were prepared each from the resin and the metal chelate compound listed in Table 1, in which the amount of the chelate compound is in part per 100 parts of solids of the resin.

Table 1

Composition	Example								Comparative Example
	1	2	3	4	5	6	7	8	
Resin (Prep. Ex.)	I-1	I-1	I-1	I-2	I-3	I-4	I-4	I-1	I-5 I-5 I-6
Chelate compound	Tris(acetyl- acetato)- aluminum		Tetrakis(acetyl- acetato)- zirconium					Diisopropoxy- bis(acetyl- acetato)- titanate	Tetrakis(acetyl- acetato)- zirconium
Amount of chelate compound	1	5	1	1	1	1	5	1	1 5 1



The following tests were conducted.

Coating property tests

The compositions of Examples 1 to 8 and Comparative Examples 1 to 3 were applied to panels to a dry thickness of 100  $\mu$  (or 50  $\mu$  for determining resistance to water and weather), dried under the conditions listed in Table 2 and then tested.

- \* Appearance: The appearance of the coating was checked with the unaided eye for gloss and faults such as shrinkage, cracking, etc.
- \* Gel fraction ratio: the dried coating on the panel (glass panel) as separated therefrom was subjected to extraction with acetone at the reflux temperature for 6 hours using a Soxhlet extractor, and thereafter checked for the ratio of the residue(%).
- \* Impact resistance: A 500-grm weight was dropped onto the coated surface of the panel (soft steel panel) using a Du Pont impact tester to determine a maximum distance of fall (cm) at which the coating remained free of cracking or scaling.
- \* Water resistance: The coated panel (soft steel panel) was immersed in hot water (40°C) for 60 days and thereafter checked for changes in the coating.
- \* Weather resistance: The coating on the panel (aluminum panel) was subjected to the cycle of irradiation with

light at a temperature of 40 to 70°C (for 15 minutes) and condensation (15 minutes) repeatedly for 2,000 hours using a QUV weather meter (product of the Q panel, UV fluorescent lamp "No. QFS-40, UV-B," wavelength range 320-280 nm), and was checked for the deterioration of the coating.

- \* Elongation: Using TENSILON UTM-II (TOYO BALDWIN CO. LTD.), the coating (5 mm in width, 20 mm in length and 50 to 100  $\mu$  in thickness) was pulled at a rate of 2 cm/min to measure the resulting increase in the length (length when broken - initial length). The elongation(%) was given by:

$$\frac{(\text{Length when broken} - \text{Initial length}) (\text{mm})}{\text{Initial length (mm)}} \times 100$$

Table 2 shows the result.

Table 2

Item	Example				
	1	2	3	4	5
Drying condition	120°C	100°C	120°C	120°C	120°C
	10 min.	30 min.	10 min.	10 min.	10 min.
Proterty test					
Appearance	Good	Good	Good	Good	Good
Elongation	85	62	90	120	45
Gel fraction ratio	98.0	97.6	96.6	95.8	99.0
Impact resistance	50 <	50 <	50 <	50 <	50 <
Water resistance	Good	Good	Good	Good	Good
Weather resistance	Good	Good	Good	Good	Good

Table 2 (continued)

Item	Example			Comparative Example		
	6	7	8	1	2	3
Drying condition	120°C	100°C	120°C	120°C	100°C	120°C
	10 min.	30 min.	10 min.	10 min.	30 min.	10 min.
Property test						
Appearance	Good	Good	Good	Good	Good	Shrinkage, cissing
Elongation	225	200	82	15	10	100
Gel fraction ratio	89.5	92.2	96.5	98.8	97.6	93.6
Impact resistance	50 <	50 <	50 <	30	50 <	50 <
Water resistance	Good	Good	Good	Good	Good	Good
Weather resistance	Good	Good	Good	Good	Good	Good

Resin (II) having alkoxyasilane group and/or hydroxysilane group

Preparation Example II-1

Phthalic anhydride	148 parts
Trimethylolpropane	27 parts
Neopentyl glycol	114 parts

The above mixture was placed into a reactor equipped with a rectification column, heated to gradually increase the temperature of the mixture to 230°C over a period of 2 hours, and then heated at the same temperature for 7 hours for dehydration condensation reaction to obtain a reaction mixture. The reaction mixture was then dissolved in a solvent mixture of xylene and butyl acetate (1:1 in ratio by weight) to obtain a polyester solution containing 50% of solids (containing 0.73 mole of hydroxyl group per 500 parts of the solution)

The above polyester solution (50% solids)	500 parts
Penyltrimethoxysilane	100 parts
Tris(acetylacetonato)aluminum	0.5 part

Next, the above mixture was placed into a reactor having a rectification column and heated at 80 to 100°C for 5 hours for reaction while distilling off methanol produced as a by-product, giving a resin II-1 containing 57% of solids (with 3.0 moles of methoxysilane

group per kilogram of the resin solids, 3,500 in number average molecular weight).

Preparation Example II-2

"Placel 208" (brand name, product of Daicel Ltd., polycaprolactone with terminal hydroxyl group, 830 in molecular weight)	95 parts
Butyl acetate	60 parts
Toluene	60 parts
Tetramethoxysilane	180 parts
Tetraisopropyl titanate	0.2 part

The above mixture was placed into a reactor having rectification column and heated at 80 to 100°C for 3 hours for reaction while distilling off methanol as a by-product. With addition of 4.0 parts of deionized water and 0.001 part of 88% formic acid, the mixture was further distilled at 80°C for 3 hours to remove the by-product, i.e., methanol, giving a resin II-2 (containing 3.8 moles of alkoxysilane and hydroxylsilane groups per kilogram of the resin solids, about 900 in number average molecular weight).

Preparation Example II-3

50% Acrylic resin (styrene/methyl methacrylate/n-butyl acrylate/2-hydroxyethyl acrylate = 20 parts/	90 parts
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30 parts/15 parts/35 parts, as  
dissolved in butyl acetate/toluene  
(1/1 by weight), 20000 in number  
average molecular weight)

$\text{OCNC}_2\text{H}_4\text{Si}(\text{OCH}_3)_3$  10 parts

The above mixture was reacted at 80 to 100°C.

Upon recognizing by IR analysis that the absorption at  
about  $2250\text{ cm}^{-1}$  due to the isocyanate group disappeared, a  
resin II-3 containing 55% solids was obtained (with 1.5  
moles of methoxysilane group per kilogram of the resin  
solids, about 25,000 in number average molecular weight).

Preparation Example II-4

60% Acrylic resin (styrene/methyl 80 parts  
methacrylate/n-butyl acrylate/  
m-isopropenyl- $\alpha,\alpha$ -dimethyl-benzyl  
isocyanate = 20 parts/20 parts/40 parts/  
20 parts, as dissolved in butyl  
acetate/toluene (1/1 by weight);  
16000 in number average molecular weight)

$\text{HOC}_2\text{H}_4\text{Si}(\text{OC}_2\text{H}_5)_3$  0.5 part

The above mixture was heated at 80°C for 5  
hours, and thereafter heated at 80 to 100°C with addition  
of 16 parts of n-butanol until IR analysis indicated  
disappearance of the absorption at about  $2250\text{ cm}^{-1}$  due to  
the isocyanate group, affording a resin II-4 containing

50% of solids (having 0.15 mole of ethoxysilane group per kilogram of the resin solids, 16000 in number average molecular weight).

Oxirane-containing resin (III)

Preparation Example III-1

Tolylene diisocyanate	174 parts
Butyl acetate	242 parts

Glycidol (74 parts) was added dropwise to the above solution at 25 to 30°C over a period of 2 hours, and the mixture was thereafter maintained at the same temperature for 3 hours, giving an isocyanate-containing oxirane compound having a solids content of 50% (with 4.0 moles of isocyanate group per kilogram of the solids thereof).


Polyester solution used in Preparation Example II-1 (50% solids)	500 parts
Above isocyanate-containing oxirane compound (50% solids)	350 parts
Dibutyltin dilaurate	0.05 part

The mixture was reacted at 75 to 80°C until IR analysis revealed disappearance of the absorption at around  $2250\text{ cm}^{-1}$ , giving a resin III-1 having a solids content of 50% (with 1.6 moles of oxirane group per kilogram of the resin solids, 4500 in number average molecular weight).



Preparation Example III-2

Isophorone diisocyanate	222 parts
Butyl acetate	445 parts

The compound  $\text{HO}-(\text{CH}_2)_5-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{CH}_2-$   (223 parts)

was added dropwise to the above solution over a period of 2 hours at a temperature of 50 to 55°C, and the mixture was thereafter maintained at the same temperature for 3 hours, giving an isocyanate-containing oxirane compound having a solids content of 50% (containing 2.2 moles of isocyanate group per kilogram of the solids thereof).

Above isocyanate-containing oxirane compound (50% solids)	5 parts
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50% Acrylic resin used in Preparation	95 parts
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Example II-3

Dibutyltin diacetate	0.01 part
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The above mixture was reacted at 75 to 80°C until IR analysis revealed disappearance of the absorption at about  $2250\text{ cm}^{-1}$ , giving a resin III-2 having a solids content of 50% (with 0.11 mole of oxirane group per kilogram of the resin solids, 22000 in number average molecular weight).

Preparation Example III-3

50% Acrylic resin used in Preparation	90 parts
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Example II-4



Methyl isobutyl ketone 10 parts

Dibutyltin dilaurate 0.10 part

The above mixture was reacted at 80 to 100°C until IR analysis indicated disappearance of the absorption at about 2250  $\text{cm}^{-1}$ , giving a resin III-3 having a solids content of 50% (containing 0.8 mole of oxirane group per kilogram of the resin solids, 19000 in number average molecular weight).

#### Examples 9-14

The resins of Preparation Examples II-1 to -4 and III-1 to -3 were used in the combinations and proportions (calculated as solids) given in Table 3, along with the chelate compounds listed in Table 3 to obtain curable compositions according to the invention.

#### Comparative Example 4-6

The resin of Preparation Example II-3 was used to prepare the comparative compositions listed in Table 3.

Table 3

Composition	Example		
	9	10	11 12
Resin (II)	II-1	II-2	II-2 II-3
Amount	30	30	50 50
Resin (III)	III-1	III-2	III-3
Amount	70	70	50 50
Chelate compound	Diisopropoxy (ethylacetoacetate)-aluminum	Tris(ethyl-acetoacetate)-aluminum	Tetrakis-(acetyl-acetonato)-zirconium
Amount	1.0	0.5	2.0 2.5
			Tris(n-butyl-acetoacetate)-aluminum

Table 3 (continued)

Composition	Example					
	13	14	4	5	6	Comparative Example
Resin (II)	II-4	II-4	II-3	-	II-3	II-3
Amount	50	50	100	-	50	50
Resin (III)	III-3	III-2	-	III-3	III-3	III-3
Amount	50	50	-	100	50	50
Chelate compound	Tetrakis-(n-propyl-acetoacetate)-zirconium	Tris(n-butyl-acetoacetate)-aluminum	Tris(n-butyl-acetoacetate)-aluminum	Tris(n-butyl-acetoacetate)-aluminum	Tris(n-butyl-acetoacetate)-aluminum	-
Amount	1.5	1.0	2.5	2.5	-	-

#### Coating property tests

The compositions of Examples 9 to 14 and comparative Examples 4 to 6 were applied to panels to a dry thickness of 100  $\mu$  (or 50  $\mu$  for determining resistance to water and weather), dried under the conditions listed in Table 4 and tested for appearance, gel fraction ratio, impact resistance, water resistance and weather resistance in the same manner as described above.

The coatings were also tested for pensile hardness according to JIS K-5400.

Table 4

Item	Example			
	9	10	11	12
Drying condition	100°C	100°C	60°C	24°C
	30 min.	30 min.	30 min.	24 hr.
Property test				
Appearance	Good	Good	Good	Good
Pencil hardness	H	H	2H	HB
Gel fraction ratio	90.1	96.1	92.7	90.5
Impact resistance	50	> 50	> 50	50
Water resistance	Good	Good	Good	Good
Weather resistance	Good	Good	Good	Good

Table 4 (continued)

Item	Example		Comparative Example			
	13	14	4	5	6	
Drying condition	80°C	100°C	100°C	100°C	100°C	
	30 min.	30 min.	30 min.	30 min.	30 min.	
Property test						
Appearance	Good	Good	Shrinkage	Good	Good	
Pencil harness	H	2H	B	Tacky, 6B<	Tacky, 6B<	
Gel fraction ratio	95.1	95.8	31.6	0	10	
Impact resistance	> 50	> 50	< 10	Not measurable	Not measurable	
Water resistance	Good	Good	Blushing, blistering	Not measurable	Not measurable	
Weather resistance	Good	Good	Dulling, cracking	Not measurable	Not measurable	

CLAIMS:

1. A curable composition characterized in that the composition comprises:

- (i) a resin (I) having an alkoxyasilane group and/or hydroxysilane group and oxirane group and obtained by reacting a resin (A) having at least one functional group selected from among an isocyanate group, hydroxyl group, oxirane group, carboxyl group and amino group with a compound (a) having a functional group complementary to and reactive with the functional group of the resin (A), and an alkoxyasilane group and/or hydroxysilane group and with a compound (b) having a functional group complementary to and reactive with the functional group of the resin (A) and oxirane group, or
- (ii) a mixture of a resin (II) having an alkoxyasilane group and/or hydroxysilane group and obtained by reacting the resin (A) with the compound (a) and a resin (III) having oxirane group and obtained by reacting a resin (B) having a least one functional group selected from among an isocyanate group, hydroxyl group, carboxyl group and amino group with the compound (b), and
- (iii) a chelate compound serving as a crosslinking curing agent and admixed with the resin (I) or the mixture.

2. A curable composition as defined in claim 1



wherein the resin (I) is a resin containing a urethane bond.

3. A curable composition as defined in claim 1 wherein at least one of the resin (II) and the resin (III) is a resin containing a urethane bond.

4. A curable composition as defined in claim 2 wherein the resin (I) is a resin containing a urethane bond and having as functional groups about 0.01 to about 10 moles of the alkoxy silane and/or hydroxy silane and about 0.1 to about 10 moles of the oxirane per kilogram of the resin.

5. A curable composition as defined in claim 3 wherein the resin (II) is a resin containing a urethane bond and having as functional group(s) about 0.01 to about 10 moles of the alkoxy silane and/or hydroxy silane per kilogram of the resin.

6. A curable composition as defined in claim 3 wherein the resin (III) is a resin containing a urethane bond and having as a functional group about 0.1 to about 10 moles of oxirane group per kilogram of the resin.

7. A curable composition as defined in claim 1 wherein the resin (I) or (III) is a resin having an alicyclic oxirane group.

8. A curable composition as defined in claim 1 wherein the chelate compound is present in an amount of

about 0.01 to about 30 parts by weight per 100 parts by weight of the resin component (i) or (ii) calculated as solids.

9. A curable composition as defined in claim 1 wherein the chelate compound is at least one of an aluminum chelate compound, zirconium chelate compound and titanium chelate compound.

10. A method of curing the composition as defined in claim 1 characterized by curing the composition at a temperature of up to 100°C in the presence of water.